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CONCERNING THE REACTIVITY AND CONJUGATION OF THE φ -OLEFINS

By I.L. Knunyants

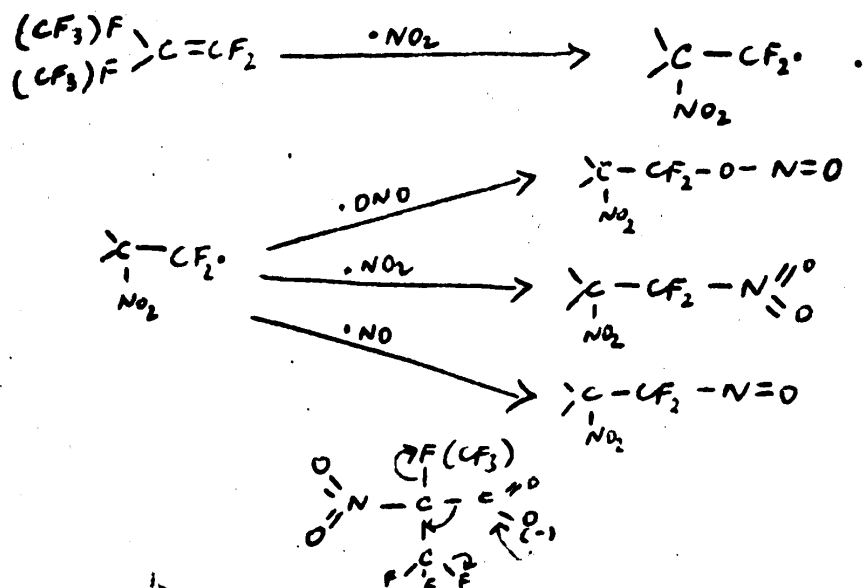
The specific properties of the φ -olefins reflected most strikingly in their reactions with nucleophilic reagents have now ceased to astonish chemists, since these properties are accounted for by the electronic exhaustion of the π -bond. According to their speed of interaction with nucleophilic compounds, the φ -olefins may be arranged in a row, with φ -ethylene the least reactive.

The reverse holds true in reactions with electrophilic compounds. The same relationships are valid in radical reactions, which proceed the more readily, the weaker the bond of the reagent forming the radical. Noteworthy in this respect are the reactions of the φ -olefins with nitrogen dioxide, in which, apart from the dinitrocompounds reported by Cofman in 1949 and Haszeldine in 1953, exceedingly interesting nitrites of β -nitroperfluor paraffin alcohols and β -nitroperfluornitroparaffins could be formed.

Investigation has shown that in these reactions, which are of a radical nature, the reactivity of the φ -olefins, as might be expected, falls drastically from φ -ethylene via φ -propylene and φ -cyclobutene to φ -isobutylene. Thus, whereas tetrafluoroethylene reacts with N_2O_4 explosively and a controlled reaction can be obtained only in the medium of an inert solvent (CCl_4 ; CH_2Cl-CH_2Cl , etc.). φ -isobutylene can be drawn into the reaction only at 160 - 180°C. without the use of a solvent. In every case, along with dinitro- φ -paraffins there do indeed appear nitrites of β -nitro- φ -paraffin alcohols, whose formation earlier investigators somehow failed to notice. When φ -ethylene, φ -propylene, and φ -iso-butylene are nitrated, the ratios of the dinitroparaffins and the nitrites formed are 1:1, 1:4, and 1:1 respectively.

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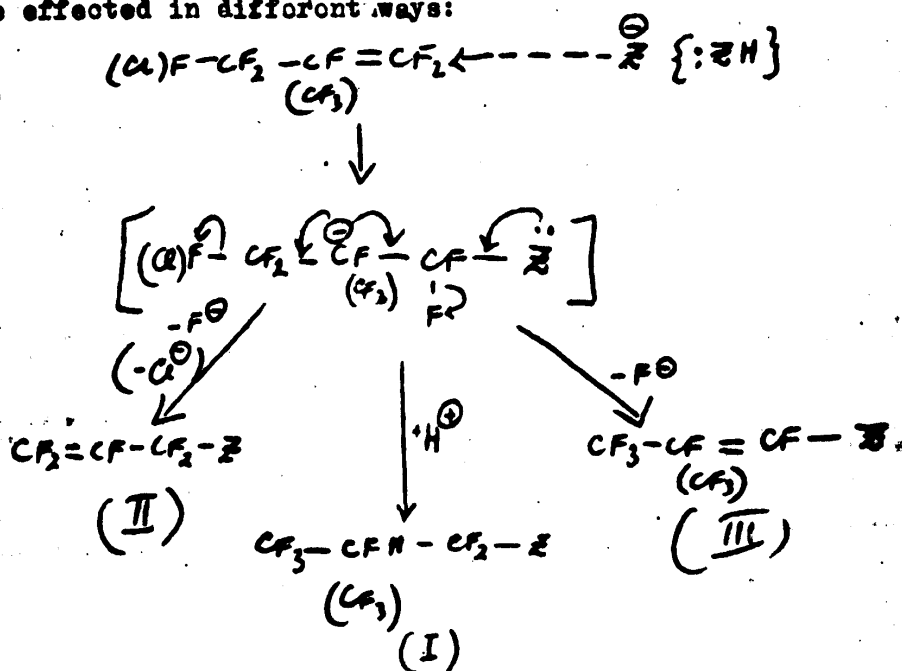
The reaction begins with the Ψ -olifine being attacked by the radical-like electrophilic particle NO_2 and leads to a radical stabilized by the interaction of the odd electron with C-F bonds, which Hasseldine rightly compares in stability with tertiary radicals. The further recombination of these radicals gives rise to nitrites and nitrosocompounds:



The nitrites of β -nitro- Ψ -paraffin alcohols formed are stable liquids with low boiling points (the nitrite of β -nitroethanol boils at 17° ; propanol, at 57° , and isobutanol, at 48°). They are very easily hydrolyzed into corresponding α -nitro- Ψ -paraffin carbonic acids, which, unlike the hydrocarbon α -nitro acids, are exceedingly stable with respect to heating. For instance, $\text{CF}_2\text{NO}_2\text{-COOH}$ is distilled without any decomposition at 80° (31 mm.); $\text{CF}_3\text{-CFNO}_2\text{-COOH}$, at 119° (760 mm.), and $(\text{CF}_3)_2\text{CNO}_2\text{-COOH}$, at 151° (94 mm.). The stability of these acids is due to the impossibility of achieving a saturated state with a negative charge on the oxygen atom of the nitrogroup, owing to the electron-constricting effect of the fluorine atoms and the methylenic groups which are in an α -position with respect to the carboxyl (diagram 1).

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A closer examination of this interesting type of unsaturated compounds thus reveals specific features of their reactivity, which are often a result of the effect of C-F bond conjugation. However, the phenomenon of bond conjugation is borne out most strikingly by the reactions of the Ψ -olefins with nucleophilic reagents. These reactions reveal the existence of conjugation not only in the non-reacting molecule of the Ψ -olefine, but also in the intermediate ions and transient complexes formed in the nucleophilic attack. The attacking particle of the nucleophilic reagent, the ion or molecule carrying a free pair of electrons approaches the carbon atom of the Ψ -olefine with the least electron density. The static bond conjugation in this case begins to acquire a dynamic character, which is adequately designated by the transcription of an ion, which actually represents one of the saturated states of the reaction intertwinement. The stabilization of this ion can be effected in different ways:



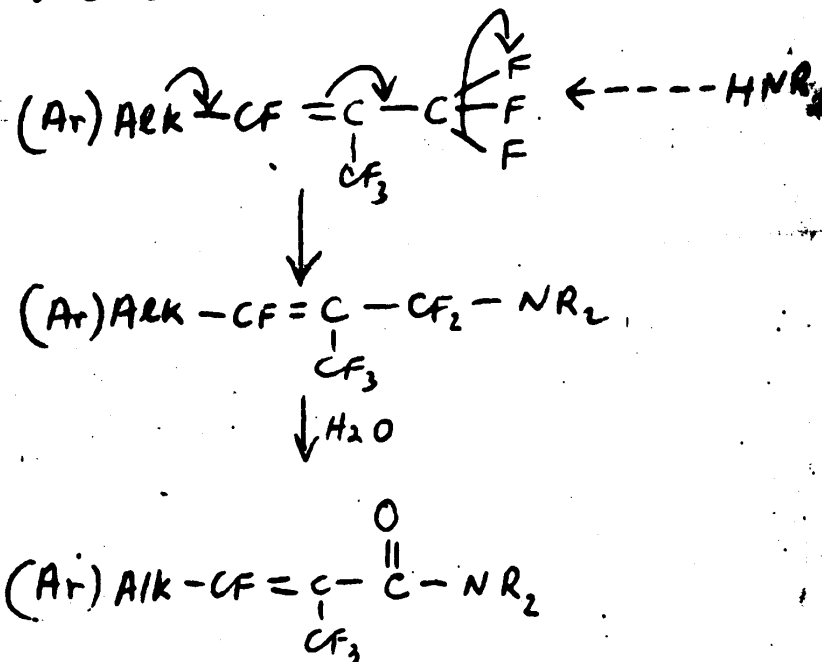
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- 1) combination with a proton to form a saturated compound;
- 2) elimination of a halogen atom of the trifluoromethyl group to form a product of alkyl substitution (II);
- 3) elimination of a fluorine atom from the alpha-position with respect to the substituting agent to form a product of vinyl substitution (III).

The last process takes place owing to the double conjugation in the intermediate ion: a) of the negative charge with the C-F bond, and b) of the p-electrons of the substituting agent with the same C-F bond.

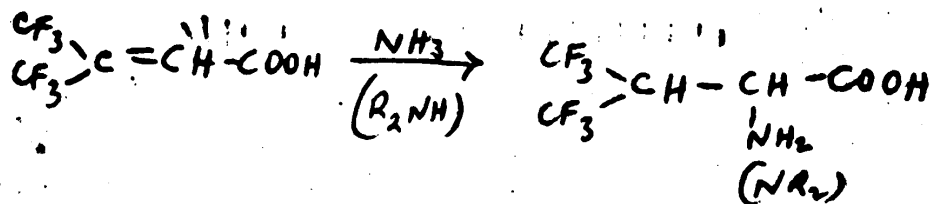
The tendency to form unsaturated compounds increases with the mobility of the electron pair of the attacking reagent and with the degree of dispersion of the negative charge in the intermediate ion. When secondary amines act on γ -ethylene, γ -propylene, and γ -isobutylene, the products of combination and vinyl substitution are thus formed in the ratios of 1:0, 0.7:0.3, and 0:1 respectively.

It is noteworthy that when amines act on perfluoroisobutylenes with an alkyl or aryl radical in position 1, we observe only the substitution of the fluorine atom in the trifluoromethyl group, which is a result of the conjugation of the C-F bond in the trifluoromethyl group with the multiple bond in the non-reacting molecule.

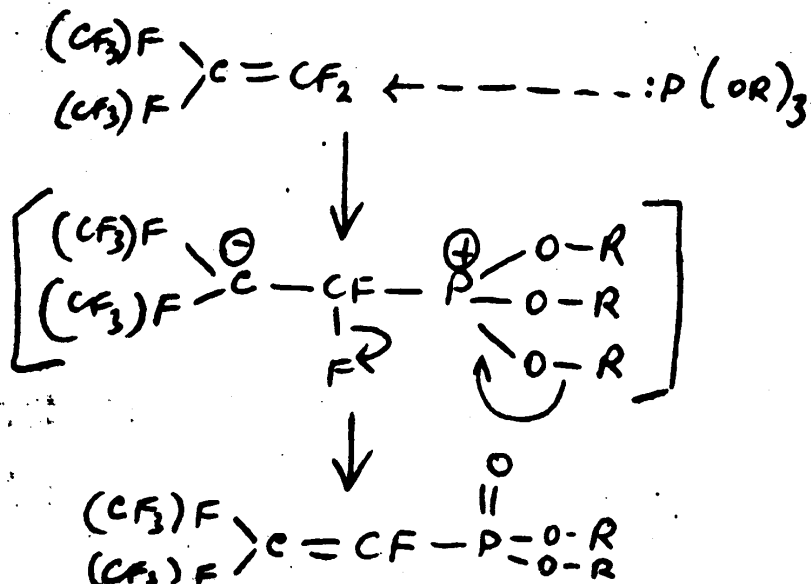


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However, when an electron-donor substitute is replaced by an electrophilic one in position 1 in the molecule of fluorisobutylene, the general conjugation of the system is dislocated. Thus, β, β' -ditrifluormethylacrylic acid with secondary amines forms only products of addition, and, since the electrometric effect ($-E$) of the carboxyl group proves weaker than the inductive effect ($-I_s$) of the two methforilic groups, the addition of ammonia and the amines produces only hexafluorvaline and its derivatives.



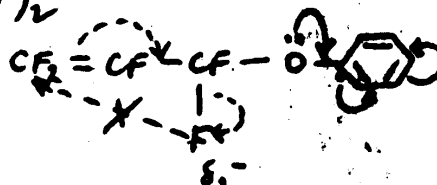
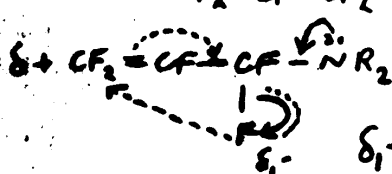
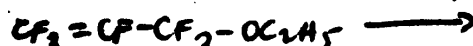
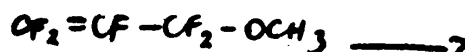
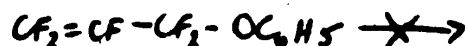
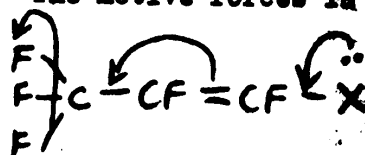
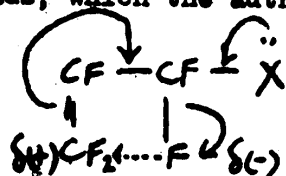
An interesting new instance of nucleophilic substitution in the fluorolefins is their reaction with trialkylphosphite, recently demonstrated by the author of the present paper:



This peculiar case of the Arbuzov rearrangement furnishes extra proof that the attack of an uncharged particle with an undivided electron pair can be the primary act in the interaction of a fluorolefine with a nucleophilic reagent.

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Another striking instance of the different bond conjugation effects of the Ψ -olefines is afforded by the anionotropic rearrangement of perfluorallyl compounds into perfluorpropenyl compounds, which the author observed. The motive forces in this

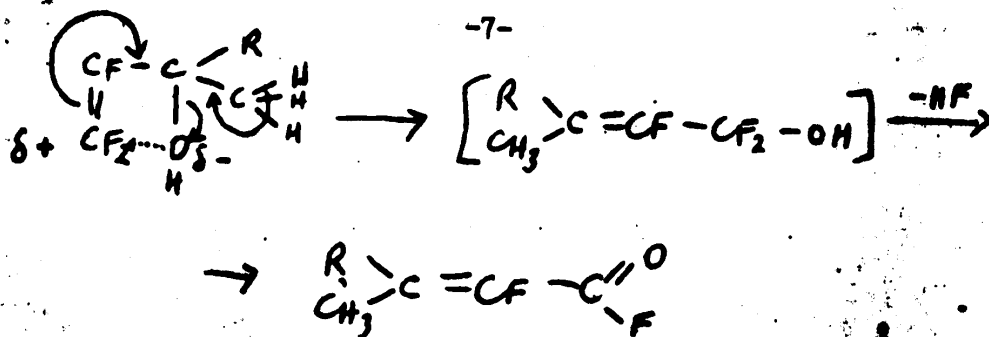


rearrangement are, on the one hand, the negative charge of the fluorine atom in the α -position, and, on the other, the positive charge of the γ -atom of the carbon.

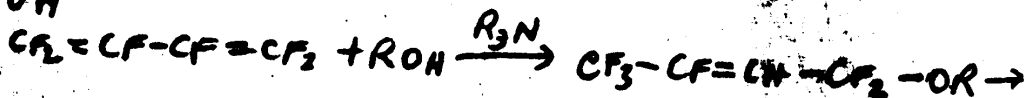
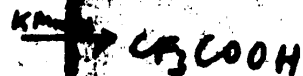
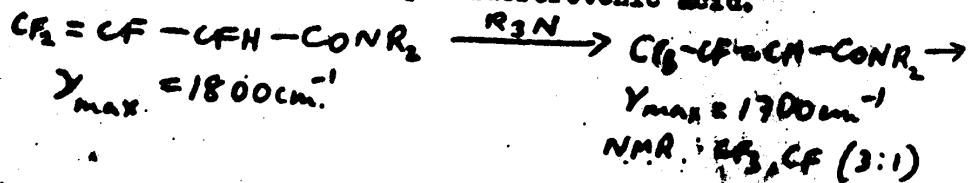
The tendency towards such a rearrangement rises with the ability of the undivided electron pair of the substitute in the allyl position. What is more, the perfluorpropenyl compound formed is energetically more stable, owing to the conjugation of the undivided electron pair of the substitute with the multiple bond and then with the C-F bond in the trifluoromethyl group.

The structure of the rearrangement products has been demonstrated by obtaining the ester of α -bromoperfluorpropionic acid, formed by the saponification of the bromination product of the methylperfluorpropenyl ester.

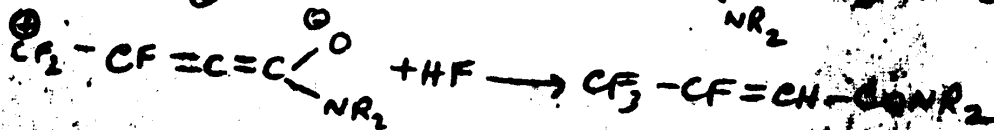
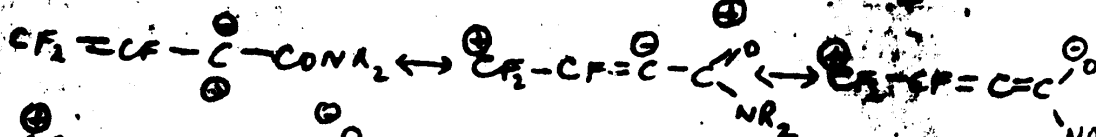
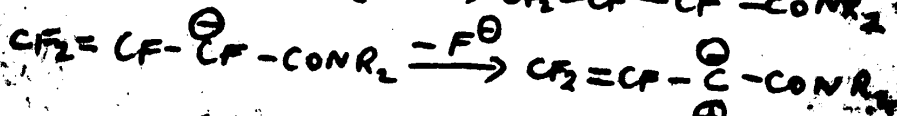
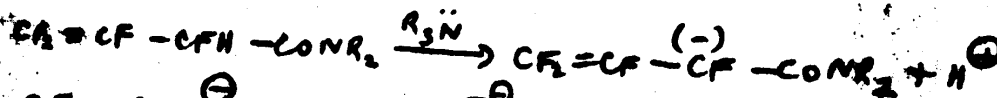
The exceedingly ready rearrangement of tertiary carbinols containing the perfluorvinyl group of atoms into fluoranhydrides of α -unsaturated carbonic acids, likewise established by the author, proceeds along identical lines.

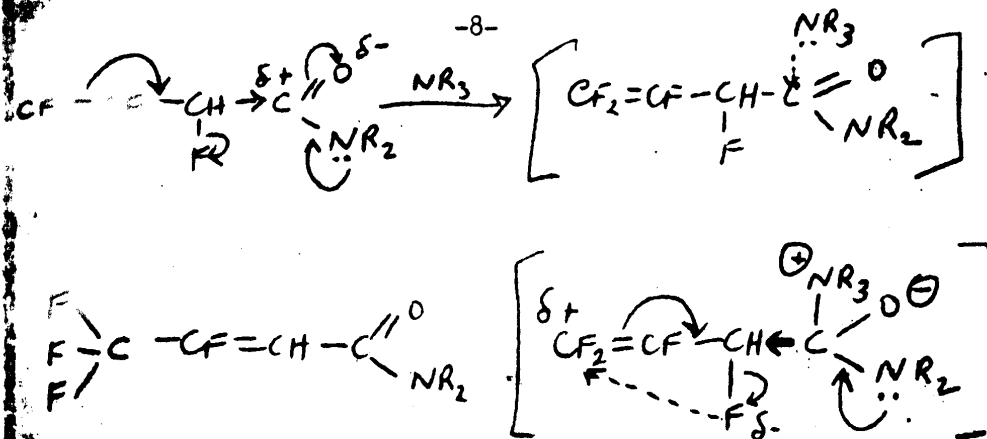


Very similar to the above in character is the rearrangement observed of the amides of alphahydroperfluorvinylacetic acid, formed by the action of diethylamine on γ -butadiene. Under the catalytic action of tertiary amines, these compounds undergo isomerisation into amides of alphahydroperfluoracetic acid.



Two probable mechanisms can be suggested for this unusual isentropic rearrangement, which is catalysed not by an acid, but by a base.





The reactions of the γ -olefines with nucleophilic reagents
 thus furnish instances of all the types of conjugation predicted
 by the theory.

The results of the investigations have been published in:

1. AHCCCF N 12, 1957, 1439

2. " N 11, 1956, 1353

N 3, 1958, 648

4. AHCCCF 114, 1957, 320

5) 1958, N 4, 540

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AROMATIC FLUORINE COMPOUNDS.

A convenient method of preparation of 2:4-dinitro fluorobenzene and some other fluoro compounds is a reaction of the corresponding aromatic chlorocompounds (containing two activating groups in o- and p- positions to a chlorine atom) with anhydrous potassium fluoride (without any solvent). This method is inapplicable for the preparation of aromatic mononitro-fluorobenzene. We have found that caesium fluoride is far more reactive in this reaction than potassium fluoride. By heating o- and p-chloronitrobenzenes with anhydrous caesium fluoride, we obtained in good yield the corresponding fluoronitrocompounds. The reaction may have some preparative value because caesium fluoride is readily re-generated from caesium chloride by means of ion exchange resins.

Some reactions of fluoronitro-compounds in which the fluorine atom remains in the aromatic nucleus have been investigated. The action of chlorine at high temperature (about 200°C) leads to the substitution of nitro-groups by chlorine. Thus, from 1,3 difluoro,4,6 dinitrobenzene, there was obtained 1,3 difluoro 4,6 dichlorobenzene and 2,4,5 tri-chloro-fluoro-benzene was obtained from 1-chloro-3-fluoro,4,6 dinitrobenzene. By the action of chlorine on 2,4 dinitro,fluorobenzene there was obtained 2,4 dichlorofluorobenzene and depending on the conditions, various yields of fluoro-chloro-nitrobenzenes (mostly 2 chloro 4 nitrofluorobenzene). The nitration of 2,4 dichloro-fluoro-benzene, gave 2,4 dichloro 5 fluoro-nitrobenzene. By the action of anhydrous caesium fluoride on this compound, there was obtained 2,4,5, trifluoro nitrobenzene.

The reduction of this compound by hydrogen with palladium black as catalyst, gave 2,4,5 trifluoro-aniline.

The reduction by hydrogen with catalysts is applicable to the most reactive fluoro-compounds. From 2,4 dinitro fluoro-benzene, we have prepared 2,4 di-aminofluorobenzene.